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2,996,412

## ART OF DEPOSITING METALS

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This invention relates to the art of depositing materials by evaporation in vacuum in the presence of the substrate to be coated, and is more particularly concerned with a method of making a vaporizer element therefor, the vaporizer so made, and the employment of such vaporizer.

This application is a continuation-in-part of my copending patent applications Serial No. 551,086, filed December 5, 1955, and Serial No. 556,358, both now abandoned, filed December 29, 1955.

There are many proposals and practices of heating a metal such as aluminum in vacuum so that the vapors are brought onto and form a coating on a substrate. Sometimes this is a purely batch operation; for example, the substrate is an article, which is placed in a bell jar with an electrically heatable filament in contact with a mass of the metal; the jar is sealed and evacuated, the filament is heated to flash metal to vapor and produce the deposit, the jar vacuum is released, and the article removed; wherewith a long life of the filament is not critically important. It has also been a practice to provide the substrate as a rolled web, to provide a vaporizer element heated as by its electrical resistance, to bring the coating material to the element so that it is melted and vaporized, and to unwind and move the substrate through the vapor and re-wind it within the evacuated space; here the life of the element must be at least long enough so that the web of substrate is coated before the seal is broken, and a life for several such operations is desirable. Also, fully continuous operations are desirable, in which the web or other long substrate is fed through a seal into an evacuated coating chamber for the coating operation, and then withdrawn through an outlet seal and collected externally of the chamber; in such cases, a very long life of the vaporizer element is necessary, because "down time" of the apparatus for replacement of vaporizer elements is highly undesirable on an economic basis and because the vaporizer element should have a regularity of output of vapor over a long period of time for producing uniformity of coating on the substrate.

A simple procedure is to employ a resistance element with a metal or carbon base, and exhibit the molten deposit in material thereon: but the efficient life of such elements has been short, for example, in some cases an hour or so and in other cases less than an hour. A common basic body for a vaporizer element is carbon, particularly when the body is to be heated by its electrical resistance to a current passing therethrough. However, carbon is subject to attack by many materials which it is desirable to deposit. For example, aluminum attacks a carbon surface, with production of carbide.

For the coating of long continuous strips and strands of material, moving at a proper rate for the specified deposition thereon, it is necessary that a supply of the molten material be maintained for a long time at a proper evaporation temperature, and therewith the vaporizer must not be so degraded during the necessary time of operation that it no longer functions.

According to the present invention, the molten material is maintained in a thin film capable of regular evaporation without the formation of bubbles and the discharge of larger masses of the material; by the employment of a heating procedure in which a part of the area

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is so devised that it permits and assures the formation of the effective film by a wetting action between the molten material and the substance providing such area. Other parts of the heated surface are so devised that they are not wetted by the molten material but tend to repel the same and are purposefully heated to a relatively lower temperature so that radiation effects therefrom are minor.

Further, according to this invention, a refractory body which is subject to attack by the molten or vaporous material, is protected by the presence of an intervening barrier layer or film of a substance highly resistant to such attack, specifically refractory borides of transitional metal elements belonging to the IV-A, V-A, and VI-A groups of the periodic system. For example, the borides of zirconium, titanium and hafnium are practically not attacked or dissolved by molten aluminum; and can provide a barrier film or layer upon a carbon body which prevents attack by molten aluminum upon the carbon body, and which itself has a long operational life. The borides of columbium, tantalum and tungsten are likewise capable of use for example during heating and evaporation of aluminum and other metals having a vapor tension like or lower than that of aluminum, and having similar or lower relative solvent power for the boride. Molybdenum and chromium borides can be employed with materials having effective vaporization velocities at temperatures far enough below that of the boride melting point so that the boride remains in place without significant loss by vaporization or by erosion due to solubility or metathesis. However, it will be understood that the borides of said families of elements are refractory, i.e., of high melting point, and are highly resistant to chemical attack; and that they may be employed as individuals or in mixtures up to their respective melting points or their development of significant vapor tension, with many deposition materials.

When the material is to be exhibited, during vaporization, in the form of a thin film, it is preferable to provide a surface for contact by the material which is readily wetted by the molten material so that a regular film is established with quick spreading of the material as it melts. Accordingly the invention includes the provision of a composite vaporizer element in which a wettable surface is presented, and the molten material in contact with this surface is isolated from the underlying support by a barrier film of such boride, with the surface, barrier, and body attached together as a vaporizer unit. For example, in aluminum depositions in vacuum, the vaporizer element can have a carbon body with a layer of the boride adherent thereto, and an outer wettable surface provided by a free refractory metal or a refractory silicide. As a further example, the wettable surface can be produced by presence of an impurity (e.g. boron or a silicide, or a metal present from excess in the forming operation) in the boride mass, or by operating at temperatures at which the boride itself has the property of being wetted by the metal to be deposited (e.g. aluminum at, say, about 2100° C.). When the element is to be heated resistively, as set out in the copending application, it is preferred, with aluminum for example, to have the molten aluminum present as a film of about fifteen thousandths of an inch in thickness, rather than in droplets on a non-wettable surface and from which the uneven and individual heating of such drops often leads to explosive disintegration of the droplets rather than an even and steady evaporation of the material. A further advantage of having the molten material present as a film, with conductive materials such as aluminum, is that the electrical path through the film and its wettable supporting surface is of less unit resistance than the path through a carbon body, so that a higher current intensity is present in and adjacent the molten material

than in the carbon, wherewith the electrical current is more efficiently employed than by transferring heat from the carbon body into the molten material with the accompanying requirement of high temperature in the carbon body. Heat radiation from the carbon body is not only an economic loss, but is operationally disadvantageous when substrates of heat-sensitive substances are to be coated, such as webs or filaments of cellulosic or synthetic origin.

An object of the invention is the provision in the art of vacuum deposition of method and means whereby a limited area of the vaporizer element is effective for presentation of a film of the material to be evaporated, while other areas remain relatively free from such film.

Another object of the invention is the provision of a vaporizer element for the material to be evaporated, having thereon a limited area upon which the molten material will readily spread.

A further object is the provision of a vaporizer having differentially heated parts effective for promoting migration of the molten material toward a hotter region and for restricting movement toward a colder region.

A further object is the provision of a procedure of depositing a material in vacuum by the controlled heating of a body to different temperatures at defined parts thereof, bringing the material into a molten film formed at a hotter region of the body, and thermally controlling the movement of the molten material.

A further object of the invention is the provision of a vaporizer element having a refractory supporting body subject to attack by the material to be vaporized, and having thereon a barrier layer of a refractory boride inhibiting such contact.

A further object is the provision of a method of making such vaporizer elements.

A further object is the provision of a method of depositing a material on a substrate in vacuum, comprising supporting the material in molten form by a body subject to attack by the material to be vaporized, with interposition of a layer of a refractory boride for inhibiting contact of the material with the body, and heating the material to effect evaporation thereof in the vacuum.

Illustrative forms of practice of the invention are shown on the accompanying drawings in which:

FIGURE 1 is a section on an upright plane through a vacuum deposition apparatus according to this invention;

FIGURE 2 is an upright section through a modified form of apparatus;

FIGURE 3 is a cross-section through one form of vaporizer element;

FIGURE 4 is a section through another form of vaporizer;

FIGURES 5, 6 and 7 are sections through further modified forms of vaporizers;

FIGURE 8 is a perspective view of the vaporizer structure as shown in FIG. 3;

FIGURE 9 is a perspective view showing a vaporizer and its connection clamps upon the supplying bus bars;

FIGURE 10 is an end elevation of a clamp with a vaporizer unit therein.

FIGURE 11 illustrates in perspective a vaporizer element having a barrier film of limited lateral dimension.

In these drawings, FIGURE 1 shows a conventionalized vacuum coating apparatus including a chamber provided by a drum 10 having at its open end a flange 11 which can be sealed to an upright fixed wall 12 and so held by the bolts 13. The chamber can be evacuated by an appropriate pumping system (not shown) through a duct 14. The wall 12 supports the horizontal take-up roll 15 which is driven by means not shown. A supply roll 16 has a web or strands of metal, plastic, etc., upon which the deposition is to be performed: the illustrative web 17 is led in the direction of the arrow over the rolls

18 and 20 to the driven take-up roll 15. Also supported from the wall 12 are the pairs of bus bars 21 having clamping connectors C leading to the ends of the relatively heated evaporator elements E described herein-  
after: it will be noted that an appropriate number of such elements can be positioned beneath the traveling web 17 to effect deposit on the lower surface thereof, with the top surfaces of the elements in horizontal planes. The material to be evaporated and deposited, e.g. aluminum, is illustratively supplied as wire from reels 23, being led therefrom by the driven wire-feeding means 24 including guide tubes through which the ends of the respective wires come to the tops of the elements E near the centers of length thereof, and the material is there melted. In practice, the end of the wire is moved back and forth along the vaporizer, to within  $\frac{3}{4}$  inch from each end: this can be done by moving the feed rolls 24 correspondingly.

In FIGURE 2, the chamber is formed by walls 25, with sealable access panels 26. Partitions 27, 28 divide the chamber into a central coating compartment 29, the end supply compartment 30 and the end take-up compartment 31. In compartment 30 is the roll 16a of material to be coated, from which the illustrative web 17 moves over the guide roll 18a, thence through the slot 32 in partition 27 and thence into the compartment 29, there passing over a turning roll 19a and moving downward in compartment 29 to a turning roll 19b, thence passing through a slit 33 in partition 28 and entering compartment 31, where it moves over the guide roll 20a and is taken up on driven roll 15a. During this passage through the compartment 29, deposition can be effected simultaneously on both sides of the web from the vaporizer elements E disposed at both sides and connected to the pairs of bus bars 21 and supplied with the deposit material in wire form from the reels 23, as in FIG. 1. Here, the feed rolls 24 can be oscillated transversely of the elements E, above the layers 43. In this form, the elements E are inclined, for example at 45 degrees, with their film-presenting surfaces addressed angularly toward the traveling web 17, and the supply of material to be evaporated is delivered near the upper ends of the individual elements E. Here, also, the number of elements E, and their specific positions and locations, can be determined by the abilities to generate vapor at the required rate and at the necessary points for effecting the desired depth of deposit on one or both surfaces of the web 17.

Electric current in parallel conductors tends to flow along the path of least resistance; so that a conductor having one unit of resistance conducts twice the current as a parallel conductor with two units of resistance. The energy converted to heat can be represented by  $I^2R$ , that is, by the product of the square of the current and the resistance. A conductor of significant cross-section can be regarded as a bundle of multiple conductors each having its own resistance factor.

The heated vaporizer elements or units for the structures of FIGS. 1 and 2 may be made in various ways, illustratively as shown in FIGS. 3 to 10.

In FIGS. 3 and 8, the vaporizer element E has a carbon body shown with a flat top having a groove along its length at a central part thereof, for receiving strips 43a, 43b of a material wettable by the material to be deposited. These strips may have a thickness of  $\frac{3}{4}$ 000 of an inch, for filling the groove provided in the carbon body. The under surface of the body B is beveled from its edges, so that the body is thinner at the edge portions 41 than at the center portion 42. Thus, the electrical resistance along the center of width is less than that adjacent the longitudinal edges, corresponding to the smaller cross-section of the portions, and correspondingly a greater proportion of the total electrical energy is converted to heat along the center than at the edges,

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and therewith the top area above the center portion 42 is more highly heated.

In FIGS. 3 and 8, the ends of the body have a greater thickness, as indicated by the projections 44, to provide a proper cross-section thereat for the transmission of the electrical current to and from the element. In this form, also, a cavity 45 is provided on the upper surface of the element E, for receiving the supply of molten material, the inner ends of the strips 43a, 43b making contact with the pool of material and causing the same to spread into the evaporation film: this cavity is frequently desirable when the element is in inclined position as illustrated in FIG. 2. After a period of use of the unit of FIGS. 3 and 8, the aluminum, in spreading over the surface of the strips 43a, 43b forms a carbide with the carbon, thus bonding the strips in position and serving as a barrier against further penetration of aluminum between the strips and the body.

The evaporation zone provided by the strips 43a, 43b with the molten material forming a pool in cavity 45 and a film on the metal layer, also has less resistance than a corresponding section of the carbon body, and hence is more highly heated. The top surfaces of the edge portions 41 are cooler than the central portion 42, and are not wettable by the molten material, and hence the latter has little tendency to creep laterally toward the edges but instead the heated central portion tends to draw the molten material in a direction away from such edge portions.

In the form of structure shown in FIG. 4, the element E has a carbon body which in section has its surfaces parallel or at right angles to one another: that is, it has the form of a broad T. The edge portions 41 are thinner than the central portion 42. A layer 43 of refractory material wettable by the material to be deposited is provided opposite the central portion 42, and has a width corresponding to that of the central portion 42; the edges of the layer 43 here being spaced, as in FIG. 3, from the edges of the carbon body.

The form shown in FIG. 5 is similar to that in FIG. 3, but is non-symmetrical in that the right-hand edge portion 41 extends farther from the central wettable layer 43 than the left-hand portion 41 does. In this form, the central cavity has been omitted: a simple groove can be cut along the flat upper surface of the unit, and a strip of wettable material placed therein, extending from end to end. The non-symmetrical form is useful when pairs of bus bars are close together, because in such cases, the slow creeping of the film layer 43 toward the edges is not symmetrical, as the creepage is more in one lateral direction than the other. Correspondingly, the central portion and layer 43 can be advantageously spaced farther from one edge than from the other.

In FIG. 6, the carbon core or body 46 has a rectangular section, with the layer 43 of wettable material forming a longitudinal band for a part of the width thereof. In this construction, the molten material in conjunction with the conductive layer 43 provides a path of less resistance than that formed by the carbon core, and hence the greatest heat conversion is in the region defined by the layer or strip 43, as before, with the carbon body being less highly heated, noting that radiation from the edge portions of this body acts to reduce their temperatures.

In FIG. 7, the carbon core or body is not homogeneous, but is formed with a central portion 51 of more conductive material, while the side portions 52 are of less conductive composition, e.g. a composition having a greater proportion of low-conductive admixed substance such as aluminum oxide, kaolin, beryllium oxide, etc., not attacked by the molten film material at the operating temperature of such portions.

In FIG. 8, the element E is illustratively 5 inches long and up to 2 inches wide, having a central portion  $\frac{3}{8}$  inch thick between top and bottom surfaces; the marginal portions are tapered to about  $\frac{1}{8}$  inch thick at the edges. The terminals C at the ends can be provided by copper

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blocks 22 (FIGS. 9 and 10), which are notched for receiving the ends of the vaporizer elements E and have the copper or steel clamp plates 22a: the parts being assembled by screws 55. Since it is preferred to have the bus bars 21, close together, a part of each clamp piece 22a is cut away as shown at 56, to avoid short-circuiting. An end of an element E is received in the passage 57 provided between the block 22 and the clamp piece 22a, and is pressed in position by a clamping bolt 58 recessed into the piece 22a to avoid accidental contact or short-circuiting. Such assemblies assure satisfactory current transfer areas and sections; and are heavy and stable enough so that they retain position by gravity upon the bus bars in FIG. 1 for example, and provide place for securing bolts if desired.

The layer 43 in FIGS. 3 and 8 is formed by strips 43a, 43b of tungsten strip  $\frac{1}{2}$  inch wide.

To assure low resistance connections, it is preferred to employ a molybdenum strip 46 which illustratively is  $\frac{1}{2}$  inch wide and  $\frac{1}{16}$  inch thick, located between the upper part of the block 22 and the underlying part of the layer 43, and extending  $\frac{1}{4}$  inch along the length of the layer beyond the clamp pieces 22 and 22a. The path of least resistance in the assembly is from a contact block C through the molybdenum strip and thence along the layer 43. With this arrangement, the heating effect is largely concentrated along the layer 43: so that in practice molten film can be heated to 1400 degrees C. in service, whereas the lateral portions 42 of the body will be at temperatures ranging down to about 650 degrees C. The metal to be evaporated and deposited is quickly melted upon contact with the center portion represented by the layer 43, and rapidly spreads over its area: evaporation occurs regularly, and the vapor departs largely in the directions at right angles to the surfaces of the vaporizers, with little spreading beyond a 90 degree angle.

Illustrative forms for the element of FIG. 4 are broad T shapes, 4 or 5 inches long and  $1\frac{1}{2}$  inches wide, with a central stem portion  $\frac{1}{2}$  inch wide and  $\frac{3}{8}$  inch thick between top and bottom surfaces: the marginal portions are each  $\frac{1}{2}$  inch wide and  $\frac{1}{16}$  inch thick. The upper surface can be flat; and the layer 43 formed of tungsten silicide as described below, being symmetrically at the center and having a width of  $\frac{1}{2}$  inch and thus overlying the central stem portion.

The drawing effect, which is a factor in restricting movement of the molten material, may be noted in the general behavior of molten metal present on a differentially heated surface, wherewith the molten material tends to spread or move along the temperature gradient in the direction of the higher temperature. The present devices take advantage of this by having a middle portion of the heater at a higher temperature than the marginal areas. In the preferred forms as illustrated, the wettable area at which the film is present terminates short of the edges, wherewith the maximum heating effect is limited and defined for a central portion of the width over the general operating life of the vaporizer.

Illustrative conditions for evaporating and depositing aluminum are the employment of a pressure around 1 mu in the vacuum chamber, with the heating of the aluminum film or layer 43 to a temperature of around 1400 degrees C. therein, wherewith the vapor pressure of the aluminum is on the order of magnitude of 100 mu. Under such conditions, and by a feeding of aluminum wire at a rate for maintaining a molten film averaging about fifteen one-thousandths of an inch, there is no bubbling effect, but a regular evaporation of aluminum essentially in atomic dimensions, with these particles largely leaving the heated surface within the 90 degree angle as referred to above.

By comparison with vaporizers in which the entire top surface was heated, it was found that, when such were employed, after two hours the speed of the traveling web had to be reduced to as low as one-half of the original speed, in order to maintain uniformity of deposit, because

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only about 40 percent of the vapor was being directed within the 90 degree angle. With the above-specified heater, 93 percent was being confined within the 90 degree angle after two hours, and the speed reduction was not required.

In practice, the total heat radiation from the assembly in FIG. 3, for example, is roughly 20 percent higher than of an element having a rectangular carbon core  $\frac{1}{2}$  inch wide, with a wettable coating on the entire top surface thereof.

In each form of vaporizer structure, the carbon body provides an adequate mechanical support for the molten material. The layer 43 can be of suitable composition which is not readily dissolved or reacted by the material to be deposited, but which is wetted by such material and preferably itself is of conductive nature, for example, when aluminum is to be deposited, this layer may be formed of highly refractory carbides, borides, or silicides of tungsten, molybdenum, titanium, tantalum, columbium, zirconium, vanadium, and chromium, or of the said elemental metals themselves except chromium. Wettable refractory nitrides such as titanium and zirconium nitrides may be employed; the refractory nitrides of other metals are useful. In general, such materials are satisfactory in the deposition of many other metals and materials to be deposited: noting that the said metals, carbides, borides, silicides and nitrides are useful where the evaporation is being effected at temperatures and pressures at which the refractory material has an insignificant vapor pressure. Carbon itself has a relatively high resistance per unit sectional area, as compared to the resistance of such layers and of the molten film itself: for example, at around 1500 degrees C., the resistance of a section of carbon in a heater unit may be more than thirty times greater than the resistance of an identical sectional area of tungsten. Also, carbon is not readily wetted by molten aluminum or such metals as gold, copper, silver, etc. It is presently preferred to employ the silicides of the foregoing metals for the barrier effect, as then there is only a slow change over time by further carbidization from the carbon core, and because they can be applied very simply by use of mixed silicon and tungsten powders for example.

Another practice is to employ a composite layer: for example, silicon powder is suspended in acetone; the mixture applied to the surface of the carbon core; and the acetone expelled. A thin foil of tungsten, having a width of  $\frac{1}{2}$  inch in the specific example described for FIG. 6, is then held in place upon the silicon deposit, and the assembly heated so that a barrier and bonding interfilm of silicon compounds, particularly tungsten silicide, is formed, with the exposed surface of wettable free or elemental tungsten. As another example of practice, tungsten and cobalt powders or tungsten and chromium powders can be mixed and applied to the area of the carbon core at which the layer 43 is to be formed: upon heating, the cobalt or chromium acts as a temporary binder for holding the tungsten upon the carbon base, with a heating to fusion for example in vacuo or an inert atmosphere: a higher temperature then expels most of the binder metal, that is, that which has not itself carbidized, and the tungsten is left as an intermediate binding film of tungsten carbide with a surface of free or elemental tungsten.

As the evaporation operation is continued, for example with aluminum, small quantities of the layer material are dissolved in the aluminum and then are precipitated again as the aluminum evaporates, particularly at the colder lateral portions of the film: thus, along the periphery of the film, the precipitated material extends a little beyond the boundary of the original area of the layer. This dissolution and deposition continues and there is a gradual progression of the area occupied by such precipitated material, and therewith the wettable area gradually widens. In practice, there is some condensation of

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the evaporated material upon the elements E and their contact blocks C, but this deposit is insignificant upon element surfaces laterally outside the evaporating film: upon the parts of a contact block C where the layer 43 enters the same, e.g. over the molybdenum contact strips in FIG. 8, a building up has been noted during the course of effective life of the element with an advantage of reducing the transfer resistance to current movement between contact block and element. The life of the vaporizer is therefore determined by the lateral growth or spreading; when the affected area extends to or past the edges of the carbon core, the aluminum evaporated from the vaporizer element is not directed as before in a cone or wedge of small angle, and thus toward the material to be coated; so that a lesser coating thickness is provided upon the substrate for a given rate of supply of the illustrative aluminum to the vaporizer, and other apparatus parts receive undesired coatings. Aluminum, when molten under the conditions of vacuum deposition, e.g. at a temperature of 1400 degrees C. and a vacuum of around one mu within the chamber, has a slow solvent action upon the carbon core, with the formation of aluminum carbide as stated above, and deposition of this at the edges of the layer 43; but in practice this action is very slow so that the vaporizer elements E can operate for a long period of continuous operation or for many successive batches.

The layer 43 thus has several functions, particularly (1) regarding chemical action between the material to be evaporated and the material of the vaporizer, (2) assuring rapid spreading of the molten metal over a defined area of the vaporizer, (3) retarding spreading of the metal over the entire surface of the vaporizer, (4) assisting in procuring a maximum temperature at the defined area. Carbon itself, in the graphitic or semi-amorphous form employed for such vaporizers, is not readily wetted by aluminum and other metals and substances here employed for vacuum depositions except at excessively high temperatures: so that the aluminum, etc., does not spread out thereon.

The film of molten material is controlled so that it overlies the layer 43. The newly supplied material from the wires moving from reels 23, 23a is quickly distributed along the length and across the width of such layers 43. The lesser resistance of the element E and the molten material thereon, adjacent the portion of its width represented by the layer 43, thus causes the film to be more highly heated than at the marginal portions of the element, such as the parts 41 in FIGS. 3 and 6, and the marginal edges in FIGS. 4 and 5. With the spacing of the side edges of the layer 43 from the side edges of the carbon body, the molten material does not initially flow to the edges of the carbon body, but it is essentially confined to the area of the layer 43, and the greater heating and the higher temperature at the central area tends to retain the molten material at the center rather than to facilitate its movement toward the edges. These cooler side edges, furthermore, deliver less radiation energy, and hence have little effect in heating and causing deterioration of a thermosensitive material to be coated.

In the form shown in FIG. 11, the body 60 is of carbon and has the enlarged ends 61 by which it may be held in conductive clamps and employed as taught in my copending application for electrical resistance heating. The top of the element is shown as a plane and has, for a central part of its width and extending longitudinally for a distance permitting electrical current conduction thereto (from end to end in the illustrated form), a strip formed as described hereinafter with a top wettable surface 62 and an intervening barrier layer 63. It will be understood that the illustrative body may be 4 to 5 inches long,  $\frac{1}{2}$  inch thick and  $1\frac{1}{2}$  inches wide at the middle of width and length; with the boride film 1 to 5 thousandths thick, and the wettable surface layer 1 or 2 thousandths of an inch thick: that is, the relative thicknesses have been exaggerated for this description.

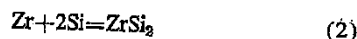
The barrier film, such as layer 63 in the drawing, which intervenes between the molten material and the attackable supporting body, consists of one or more of the aforesaid refractory borides. The top wettable surface 62, when employed, can be provided by a highly refractory, i.e. high melting point, substance wettable by the molten material to be evaporated and deposited. In coating with metals such as aluminum, the wettable surface can be provided by the metals tungsten, molybdenum, tantalum, columbium, zirconium, hafnium, vanadium and titanium; that is, the metals of the said families are useful up to temperatures at which the selected metal exhibits significant vapor tension: and such metals can be employed alone or in mixtures with one another, as silicides, in mixtures with the refractory silicides of such metals, and in mixtures of the elemental metal or metals and/or the silicides with carbides of such metals. In operation, the function of wettability is accompanied by minor solubility, so that small quantities of the substance of the wettable surface 62 dissolve into the molten material, but these are precipitated again as the material evaporates and the maximum amount in solution at any time is that which forms a saturated solution: hence an effective top wettable surface 62 remains as a permanent part of the structure.

The barrier boride layer 63 can be prepared by providing a mixture of zirconium and boron powders upon the area of e.g. a carbon body to be covered, and heating to a temperature for sintering or fusing them together (e.g. a temperature of 2500 degrees C. or above) and effecting formation of zirconium boride as a non-porous adherent film on top of the carbon. Other metals of the class, such as titanium, can be likewise employed. The reaction can be formulated as:

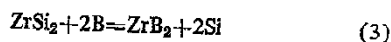


Another process of preparing the boride layer 63 is based upon reaction of silicides of the stated metals to form the corresponding borides with liberation of silicon. For this, mixed particles of the metal (e.g. zirconium), silicon and boron can be applied directly, or suspended in a volatile vehicle such as water, alcohol, acetone or the like, noting that organic liquids are volatile at below the reaction temperature, and applying a coating thereof to the area to be coated. When the support is a carbon or other conductive body, this may be heated by passing an electric current whereby to attain a temperature at which reaction is initiated between the metal and the silicon with formation of the silicide. The expulsion of the vehicle may occur in air; but it is preferred to conduct both the silicide formation and the conversion to boride in vacuum or in an inert atmosphere at reduced pressure, to restrict heat losses to radiation effects and to avoid oxide or like by-reactions at the high temperatures. The particle substances are preferably present in stoichiometric proportions, with a slight excess of silicon to assure the conversion of the metal despite any silicon loss by evaporation. The reaction is highly exothermic, and the temperature increases: the current intensity through the structure increases due to the conductivity of the silicide layer being formed, and if desired it can be increased further by raising the voltage between the terminal ends: thus quickly a surface temperature is attained at which the boron reacts with the metal silicide, illustratively zirconium disilicide) and silicon is liberated and immediately evaporates at the prevailing reaction temperature and in the vacuum. Zirconium boride remains as a hard adherent layer of high density and impermeable to the illustrative molten aluminum and essentially insoluble therein. In practice, the temperature can rise to the melting point of the zirconium boride, and therewith the coat has a gray metallic appearance.

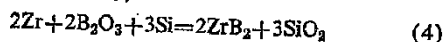
These reactions may be represented as:



with a conversion:

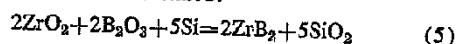


A further method is to employ mixed particles of boron trioxide, silicon, and the selected metal. The proportion of silicon should be slightly in excess of that for reducing the boron oxide and for combining with the metal as silicide. The over-all reaction can be formulated, for stoichiometry, as:



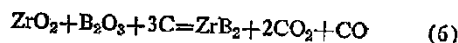
In this method, the silicon dioxide is instantaneously evaporated as it successively forms, and an end point is quickly reached with the hard impermeable coating as before.

Another method is to employ a powdery mixture of a reducible compound of the metal, boron trioxide, and silicon. Here the silicon preferably in excess acts to reduce the metal and boron compounds, wherewith the metal silicide then reacts with the boron, and the boride is produced: the silicon is converted to the dioxide which evaporates as before. The over-all reactions e.g. with zirconium dioxide can be stated:

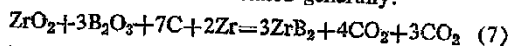


The reactions between boron trioxide and silicon, and between metal oxide (e.g. zirconium dioxide) and silicon are highly exothermic, and the generated heat facilitates the reaction with expulsion of the silicon dioxide and the deposit of the zirconium boride as a continuous film over the treated area.

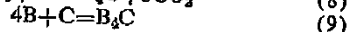
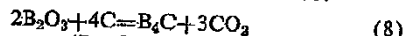
Another method is to prepare a powdery mixture of boron trioxide with the metal compound (e.g. zirconium dioxide) and carbon, which is placed on the refractory body, e.g. a carbon structure, and heated, under reduced pressure, so that reactions occur which can be stated generally:



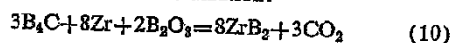
Alternatively, with use of a carbon support body whose substance can be employed for reduction, a powdery mixture of the metal compound (e.g. zirconium dioxide preferably in excess or mixed with free metal) and boron trioxide is placed upon the area for receiving the barrier film, and heating accomplished under reduced pressure, with reactions which can be stated generally:



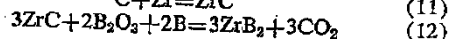
Another alternative is to provide powdery boron trioxide or boron on the surface of the carbon support, and heat under reduced pressure to form the carbide:



and then heat in the presence of the metal, either present in the original mixture or applied as powder mixed with boron trioxide after the carbidization:



Another alternative is to form the metal carbide on the surface of the carbon body, and then transform it into a boride:



In these examples, the illustrative zirconium can be replaced as free metal or the metal compound, by other elements or mixtures thereof from the IV-A, V-A and VI-A families as set out above; and the vaporizer elements made thereby employed with materials to be deposited which evaporate at reduced pressures and at temperatures at which the barrier film itself has a low vapor tension. When zirconium, titanium or hafnium metals are selected, they may be introduced in the form of hy-

drides instead of the free element, noting that the hydrides are less subject to attack by or combustion in ordinary atmosphere at room temperatures, but decompose upon heating so that, even at 300 degrees C. the hydrogen begins to escape, and the hydrogen can thus easily be expelled by heating in vacuo and can be eliminated before the respective reaction temperatures are approached.

An excess of a constituent present in refractory form with the boride barrier such as boron, or the metal, or in the form of residual unchanged silicide, can serve to attain or increase the wettability of the top surface at the operating temperature.

While the reactions have been stated on an overall basis in the equations, it will be understood that excess of one or more components may be present for the purposes stated; and that when the boron is present at below the stoichiometric proportion at the end of the reactions with metals which form multiple borides, then the barrier is composed of mixed borides, e.g. with zirconium the mono and di-borides are present.

The top wettable surface 62 can be provided by suspending a mixture of powders of silicon and one or more of the metals tungsten, molybdenum, tantalum, columbium, zirconium, titanium, hafnium, vanadium, and chromium, in water, acetone, alcohol, or other vehicle which permits spreading and can be dissipated prior to the final reactions. This suspension is spread evenly over the surface to be coated, e.g. the boride layer 63 on the carbon body 60. The structure is placed in a vacuum chamber or in an inert atmosphere preferably at reduced pressure, and warmed for expelling the vehicle, followed by higher heating under evacuation until reaction occurs and the metal silicide is formed in place upon the underlying boride barrier layer 63.

Another method of providing a top wettable layer 62 is to place upon the pre-formed barrier layer 63 a thin sheet of tungsten, molybdenum, columbium, zirconium, titanium or tantalum, for example of a thickness between 0.001 and 0.005 inch. No original bonding of the sheet is necessary; during the melting and evaporation of the material to be deposited (e.g. aluminum) any spaces are quickly filled; and upon cooling the sheet and the boride layer are found tightly joined together and to the supporting body, with re-precipitated material from the sheet adhering to the sheet and the boride layer; and after employment, the dissolution of the material of the sheet may have been total, with the re-precipitation having occurred to provide an adherent wettable layer self-bonded to the boride layer. The sheet preferably extends between the electrical terminals and forms part of the heating circuit. The barrier layer 63 need not be preformed before application of the top layer 62; care being taken to control the reaction speed so that the volatile components can escape without dislodging the material for the top layer 62.

A further method of providing a top wettable layer 62 is to mix a very high melting point metal such as tungsten, molybdenum, tantalum or other afore-mentioned metal with another of the metals or nickel or cobalt which has a melting point which is lower but yet above the temperature of employment (which may be 1400 degrees C. with aluminum deposition). The mixture may be applied as such or in a temporary suspension vehicle, over the barrier layer of boride; and then gradually heated, preferably in vacuum, until the lower melting metal sinters or fuses and forms a bond between the particles and to the barrier film. This may be employed in such form; or the temperature may be raised so that the bonding metal is caused to evaporate in vacuo, wherewith the high melting metal remains in place and bonded to the boride layer.

Also, as set out above so-called impurity can be left in the boride film for the purpose of wettability; for example by having the boron constituent low so that unconverted silicide is present, e.g. the barrier is of mixed zir-

conium boride and silicide, wherewith the silicide at the surface procures the condition of wettability.

The wettable surface 62 may be of lesser width than the barrier layer 63, as shown, when the widths are less than the periphery of the refractory support; and therewith the molten material covers the wettable layer 62 but does not pass onto the projecting parts of the barrier layer 63 when the same is not wetted under the conditions of heating, and thus the molten material does not pass onto the exposed part of the illustrative carbon body 60.

Likewise, the wettable surface can be provided in many ways. For further example, if the deposition to be effected can tolerate the presence of such surface-providing element or elements, or if a low-content alloy thereof with a deposition material is desired, then the vapor tension is of less significance or even desirable.

Such vaporizer elements of FIG. 11 can be employed in a vacuum chamber as in FIG. 1, wherewith the presence of the barrier layer protects the refractory support, e.g. the carbon body, against contact by the molten material which is being evaporated from such a vaporizer element and the vapor deposit effected upon a substrate.

It is thus possible to use carbon bodies which are of heavier section than before, with greater mechanical strength, so that the life is determined by the lateral progress of the precipitation deposition rather than by material destruction of the carbon body by the aluminum or other material to be deposited. Further, it is thus feasible to employ longer bodies with thicker carbon sections, rather than the short wide bodies of uniform electrical resistance throughout the elements of sectional areas; noting that these short wide bodies have obvious disadvantages by excessive reduction in section by corrosion, and the demand for very low voltages and very high current intensities with correspondingly large sections required for the supplying bus bars.

It is obvious that the described forms of practice are not restrictive; and that the invention may be employed in many ways within the scope of the appended claims.

I claim:

1. A vaporizer for evaporating aluminum and like materials having low vapor pressure at elevated temperatures, comprising an electrically resistive heating body of refractory substance resistive to wetting by the molten material and having along its length a lower electrical resistance at a central part of its width than at its sides and including a refractory coating presenting an outer surface wettable by the molten material and being resistant to attack thereby and located upon the said body, said coating extending along a central part of the width thereof with its side edges spaced from the side edges of the body.

2. A vaporizer as in claim 1, in which the coating is composed of a substance selected from the group consisting of the metals tungsten, molybdenum, titanium, tantalum, columbian, zirconium and vanadium, and the carbides, borides, nitrides and silicides of tungsten, molybdenum, titanium, tantalum, columbium, zirconium, vanadium and chromium.

3. A vaporizer as in claim 1, in which the heating body is of homogeneous carbon and has a relatively thick central longitudinal portion and relatively thin side portions extending therefrom, said coating being located on an upper surface of said central portion and essentially of the width thereof.

4. A vaporizer as in claim 1, in which the coating comprises a barrier film upon the body, said barrier film being selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and a surface layer upon the barrier film, the substance of said surface layer being more easily wettable than the barrier film by the material.

5. A vaporizer for evaporating aluminum and like materials having low vapor pressure at elevated tempera-

tures; comprising an electrically resistive heating body of refractory substance resistive to wetting by the said material when molten and having between its ends a cross-section with beveled surfaces extending from its edges so that the body is thinner at the edges than at a central part, and including a layer of refractory substance wettable by the molten material and being resistant to attack thereby and located upon the said body, said layer extending along a central part of the width thereof with its side edges spaced from the side edges of the body.

6. A vaporizer for evaporating aluminum and like metals having low vapor pressure at elevated temperatures, comprising an elongated electrically resistive carbon heating body having ends for electrically conductive connection and between said ends a cross-section with greater depth at a middle portion of its width than at the sides, the cross-section including a substantially horizontal upper surface portion, and a layer of refractory substance wettable by the molten metal and located on said upper surface portion and extending along the center of the width of the body from one said end to the other said end thereof and having its side edges spaced from the side edges of the body; said layer being of a substance selected from the group consisting of the metals tungsten, molybdenum, titanium, tantalum, columbium, zirconium and vanadium, and the carbides, borides, nitrides and silicides of tungsten, molybdenum, titanium, tantalum, columbium, zirconium, vanadium and chromium.

7. A composite vaporizer for evaporating aluminum and like materials having low vapor pressure at elevated temperatures, comprising an electrically resistive structure having ends for electrically conductive connection and between said ends a cross-section with a substantially horizontal top surface, a central portion of the width of said surface being wettable by the molten material and resistant to attack thereby, the side edges of the wettable portion being spaced from the side edges of said horizontal surface, the surface portions of the structure between its side edges and said central portion being resistant to wetting by said molten material.

8. The method of depositing aluminum and like materials having low vapor pressure at elevated temperatures upon an article in a vacuum chamber, which comprises locating in said chamber a heating body of substance resistive to wetting by the molten material to be deposited, said heating body being positioned with a surface directed toward the article to be coated, heating said body more highly along a central part of the width of said surface than at the side edges thereof providing upon the top of the said body and along the central part of its width a layer of refractory substance wettable by the molten material to be deposited with the side edges of the layer spaced from the side edges of the body, bringing the material to be deposited into contact with the layer for melting the material and procuring spreading of the molten material over said layer and restricting movement beyond said layer, effecting evaporation from said layer of the material to be deposited, and effecting deposition of the vapor upon the article.

9. A vaporizer for evaporating aluminum and like metals having low vapor pressure at elevated temperatures, comprising a carbon body resistive to wetting by said material when molten, and a layer thereon of refractory substance having a higher melting point than the material to be deposited and characterized in being wettable by the molten material, said layer having at selected cross-sections of the body a lesser width than the width of the top of said body at the respective cross-section whereby to restrict the area of said heater which is wetted by and upon which the molten material spreads.

10. An electrically resistive vaporizer for evaporating aluminum and like materials having low vapor pressure at elevated temperatures, comprising a carbon body and a wettable layer thereon extending along the same, said

layer having a lesser width than the periphery of the body, said vaporizer being characterized in having a greater electrical resistance along a part bare of such layer than at the part having such layer thereon.

11. For use in an apparatus for the vacuum chamber deposition of evaporated aluminum and like materials having low vapor pressure at elevated temperatures, the invention which comprises the provision in the vacuum chamber of an electrically resistive vaporizer body of carbon, a layer on a surface of said body of substance wettable by the molten material to be deposited, said layer extending in the direction of electrical flow through the body and being electrically conductive, said layer having a lesser width than the said surface of the body so that its edges are spaced from the side edges of said surface, said vaporizer body being characterized in having a greater electrical resistance along parts of the body adjacent said side edges than along said layer, and means for feeding onto said layer the material to be deposited.

12. The method of effecting deposition in vacuum of aluminum and like materials having low vapor pressure at elevated temperatures, by exhibiting the same upon a vaporizer element, the invention which comprises heating a part of the top surface of the vaporizer element for a central portion of the width thereof more highly than adjacent side portions thereof whereby to produce temperature gradients with the highly heated portion at a temperature for rapid evaporation of the material and the side portions at temperature below that of substantial evaporation at the prevailing pressure, supplying the material to be deposited to the said highly heated portion of the surface whereby the same is melted, effecting distribution of the melted material as a film over said highly heated central portion of the width of the surface for effecting evaporation thereof from the distributed film whereby the less highly heated side portions restrict creepage of the film toward the side edges of the element, and effecting deposition of the vapor upon the article.

13. A vaporizer for evaporating material in vacuum, comprising a body of refractory substance of relatively low resistance to attack by the molten material, and a coating on said body including a barrier film of substance of greater resistance to attack by the molten material and selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and a surface layer upon the barrier film, the substance of said layer being selected from the group consisting of the metals tungsten, molybdenum, tantalum, columbium, zirconium, hafnium, vanadium, and titanium, the silicides thereof, and combinations of said metals and silicides with carbides of said metals.

14. A vaporizer as in claim 13 in which the body is of carbon and is electrically conductive for resistance heating thereof.

15. A vaporizer for evaporating material in vacuum comprising a body of refractory substance of relatively low resistance to attack by the metal, and a coating on said body including a barrier film of zirconium boride and a surface layer on said barrier film of substance wettable by the molten evaporable material.

16. A vaporizer for evaporating material in vacuum comprising a body of refractory substance of relatively low resistance to attack by the metal, and a coating on said body including a barrier film of titanium boride and a surface layer on said barrier film of substance wettable by the molten evaporable material.

17. A vaporizer for evaporating material in vacuum comprising a body of refractory substance of relatively low resistance to attack by the metal, and a coating on said body including a superficial barrier film of hafnium boride and a surface layer on said barrier film of substance wettable by the molten evaporable material.

18. A vaporizer for evaporating material in vacuum comprising a carbon body, and a coating on said body in-

cluding a superficial barrier film of zirconium boride and a surface layer on said barrier film of substance wettable by the molten evaporable material.

19. A vaporizer for evaporating material in vacuum comprising a carbon body, and a coating on said body including a superficial barrier film of titanium boride and a surface layer on said barrier film of substance wettable by the molten evaporable material.

20. A vaporizer for evaporating material in vacuum comprising a carbon body, and a coating on said body including a superficial barrier film of hafnium boride and a surface layer on said barrier film of substance wettable by the matter evaporable material.

21. A vaporizer for evaporating material in vacuum comprising a carbon body and thereon a superficial barrier layer of a material selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and an outer layer of refractory material wettable by the molten vaporizable material and selected from the group consisting of the metals tungsten, molybdenum, tantalum, columbium, zirconium, hafnium, vanadium, and titanium, the silicides thereof, and combinations of said metals and silicides with carbides of said metals.

22. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a refractory body a superficial coating of boron and a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and heating the same to a temperature effective for provoking the combination of the metal and boron to form a continuous adherent metal boride coating on the surface of the body.

23. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of a mixture of boron and a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, each in divided form, and heating the same to a temperature effective for provoking the combination of the metal and boron to form a continuous adherent metal boride coating on the surface of the body.

24. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of a mixture of powders of silicon and boron and a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, heating the same to a temperature effective to initiate reaction between the metal and silicon, and then heating to a temperature effective to cause reaction between the resultant metal silicide and boron to form a continuous adherent metal boride coating on the surface of the body.

25. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of mixed powders of silicon, boron and a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, conducting electric current through the body while in vacuo whereby to heat the same and initiate reaction of the metal and silicon to form a conductive silicide coating, and maintaining the current conduction and thereby effecting a greater heating at the surface of the body whereby to initiate reaction between boron and the metal silicide with evaporation of the liberated silicon and thereby producing a continuous adherent metal boride coating on the surface of the body.

26. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of mixed powders of boron trioxide, silicon, and a metal selected from the group con-

sisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and heating the same to effect reaction with evaporation of silicon dioxide and deposition of a continuous adherent metal boride coating on the surface of the body.

27. The method of making a vaporizer for evaporation of metal in vacuum, which comprises applying to a carbon body a superficial coating of mixed powders of boron trioxide, silicon, and oxide of a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and heating the same to effect reaction with evaporation of silicon dioxide and deposition of metal boride to form a continuous adherent metal boride coating on the surface of the body.

28. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a refractory body a superficial coating of a compound of a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, and boron trioxide, with presence of carbon, and heating the same to a temperature effective for provoking reaction to form a continuous adherent metal boride coating on the surface of the body.

29. The method as in claim 28, in which the refractory body is of carbon effective to constitute at least a part of said carbon presence.

30. The method as in claim 28, in which the metal compound and boron trioxide are applied as powders mixed with carbon powder.

31. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of powdery boron trioxide, heating to produce boron carbide and continuing the heating in the presence of a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, for effecting reaction to form a continuous adherent metal boride coating on the surface of the body.

32. The method of making a vaporizer for evaporation of material in vacuum, which comprises applying to a carbon body a superficial coating of a metal selected from the group consisting of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, heating to produce the metal carbide, and continuing the heating in the presence of boron and a reducible oxide whereby to form a continuous adherent metal boride coating on the surface of the body.

33. The method of depositing material upon a substrate by evaporation of the material in vacuum, which comprises melting the material, supporting the molten material by a refractory support attackable by the molten material, maintaining between the support and the molten material a barrier formed by a substance selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, maintaining on the barrier a surface layer of a refractory substance wettable by the said material to be deposited, heating the molten material on said support to vaporize the same, and effecting deposit of the metal vapor on the substrate.

34. The method of evaporating a material in vacuum, which comprises melting the material and exhibiting the same in contact with a wettable surface of refractory substance and selected from the group consisting of the metals tungsten, molybdenum, tantalum, columbium, zirconium, hafnium, vanadium, and titanium, the silicides thereof, and combinations of said metals and silicides with carbides of said metals, said surface being supported by a carbon body and isolated therefrom by a barrier layer of substance selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic sys-

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tem, and heating the said surface to effect vaporization of the material therefrom.

35. The method of evaporating metal in vacuum, which comprises melting the metal by electrical resistance heating on a carbon body, maintaining between the molten metal and the carbon body a barrier layer of a refractory boride selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, maintaining on the barrier layer a surface layer of a refractory substance wettable by the said molten metal, and heating the carbon body for effecting vaporization of the said metal.

36. The method of evaporating aluminum in vacuum, which comprises melting the aluminum by electrical resistance heating on a carbon body, maintaining between the molten aluminum and the carbon body a barrier layer of a boride selected from the group consisting of the borides of the transitional metal elements belonging to the IV-A, V-A and VI-A groups of the periodic system, maintaining upon the barrier layer a surface of a re-

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fractory metal silicide wettable by aluminum, maintaining between the barrier layer and the molten aluminum a surface layer of refractory substance wettable by the molten aluminum, and heating said surface to effect vaporization of the aluminum therefrom.

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Aug. 15, 1961

P. ALEXANDER  
ART OF DEPOSITING METALS

2,996,412

Filed Oct. 10, 1958

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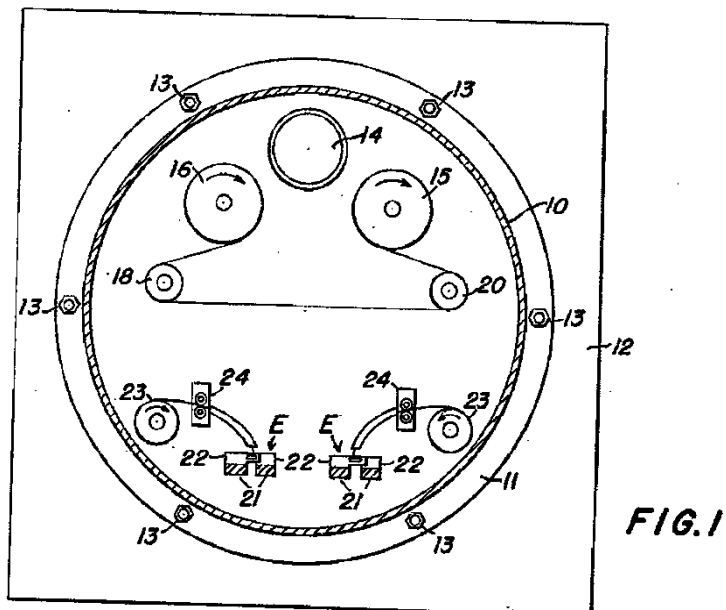


FIG. 1

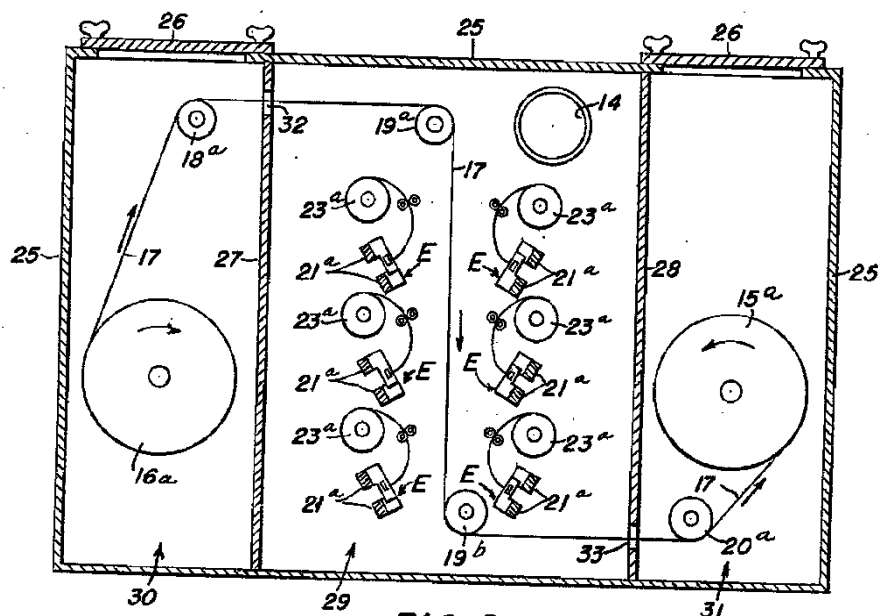


FIG. 2

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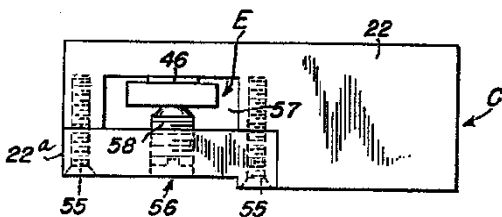
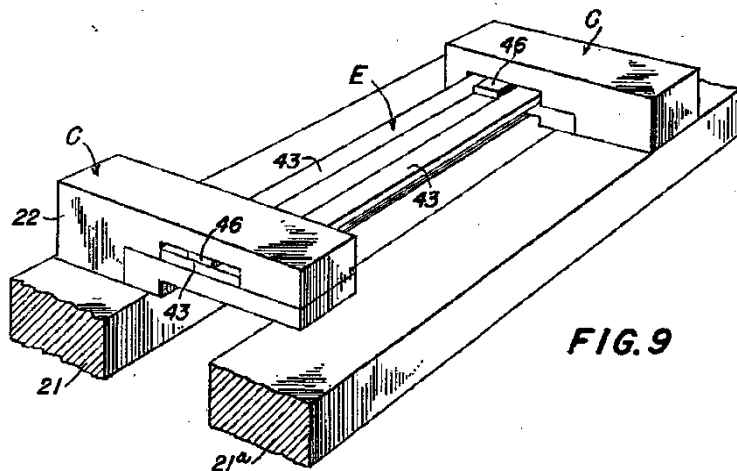
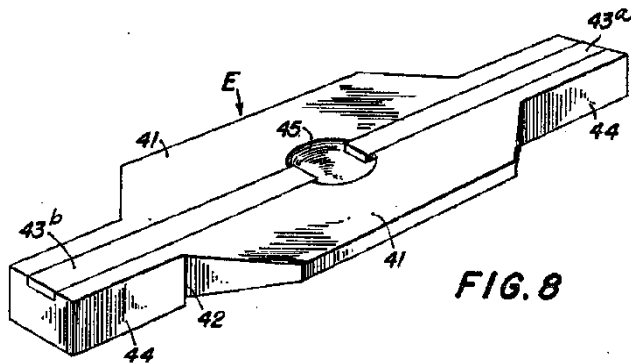
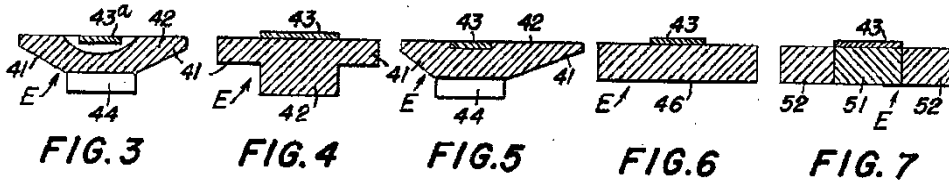
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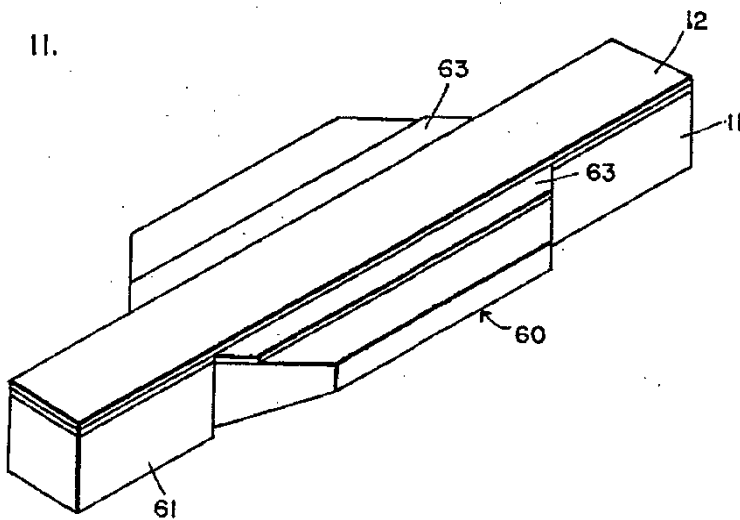
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3 Sheets-Sheet 3

FIG. 11.



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